Pervaporation of Ethanol–Organic Solvent Mixtures Through Poly(2,6-dimethyl-1,4-phenylene Oxide) Membrane

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SYNOPSIS

Homogeneous dense membranes of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) were used to separate mixtures of ethanol–organic liquid by pervaporation. If the organic liquid had a strong affinity to PPO (e.g., toluene) and its concentration in the feed was low, smaller molecules of ethanol permeate preferentially through the membrane. When the concentration of this liquid in the feed was increased up to a certain value, the membrane was, on the contrary, permeated by it preferentially. When its concentration in the feed was further increased, flux through the membrane is dramatically increased and the membrane lost its selectivity. If the liquid in a binary mixture with ethanol in the feed had a low affinity to PPO (e.g., 1-propanol), the selectivity of the PPO membrane virtually did not depend on the feed composition, and the membrane was preferentially permeated by smaller molecules. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Pervaporation is a membrane separation process in which the liquid feed mixture is circulated in contact with one side of a nonporous membrane and the permeate is removed in a vapor state from the opposite side. Due to the permselective nature of the membrane, a substance may become enriched in the permeate.

Over the past few years, pervaporation has gained widespread acceptance by chemical industries as an effective process tool for separation and recovery of liquid mixtures. Commercial systems using poly(vinyl alcohol) composite membranes for dehydrating aqueous ethanol, 1-propanol, and other organic solvents are now in use.[1] The application of pervaporation to the separation of organic–organic mixtures is relevant to chemical processing, but, in comparison with water removal from organics, its development is lagging behind. While our former studies[2,3] dealt with the pervaporation of aqueous solvents through membranes of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and its derivatives, in this study PPO membrane was used to separate organic solvent–ethanol mixtures.

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EXPERIMENTAL

Membrane Preparation

Membranes were prepared by casting PPO (Research Institute of Macromolecular Chemistry, Brno, Czech Republic, M_w = 385,000, measured by light scattering) from 5% chloroform solution. The solution was cast onto a glass plate and spread out with a casting knife. The solvent was evaporated slowly at room temperature over a few days. The membranes used in pervaporation experiments were homogeneous films 20 ± 2 mm thick.

The degree of swelling (DS) was defined as DS = $(W_s - W_0)/W_0$ where W_0 and W_s represent the weights of the dry and swollen membranes, respectively.

Pervaporation Experiments

The pervaporation apparatus consisted of a pervaporation cell with a membrane area of 43 cm^2 and a glass apparatus equipped with traps cooled by liquid nitrogen to condense the permeate. The feed mixture was circulated between the thermostatted bath (25°C) and the upstream side of the membrane in the cell. The downstream pressure was kept at 400 Pa. The compositions of the feed and of the

permeate were determined by gas chromatography and, in case of water–ethanol mixtures, by refractive index measurements using calibration curves. The total flux J at a steady state (measured approx. after 4 h from the start of the process) was obtained by $J = Q/At$ where Q is the total amount permeated during experimental time interval t and A is the effective surface area. Ethanol flux was calculated from the total flux and the permeate composition.

RESULTS AND DISCUSSION

As pervaporation is a process that combines evaporation of volatile components of a mixture with their permeation through a membrane by a solution–diffusion mechanism, its selectivity depends on the following three factors concerning the nature of the organic liquid: affinity to the membrane, bulkiness of the molecule, and vapor pressure. In particular cases various factors may accept the predominant role. It was observed[2,4] that for glassy polymers the permeability is mainly determined by the diffusivity (depending on the size of the permeating molecules) while for elastomeric polymers the solubility contribution is decisive. Pure PPO is a distinctly glassy polymer (T_g = 226°C), but when it is swollen by solvents its structure is changed. The degree of swelling of PPO in binary mixtures of liquids with ethanol used this study is shown in Figure 1.

The behaviors of trichloroethylene and of toluene

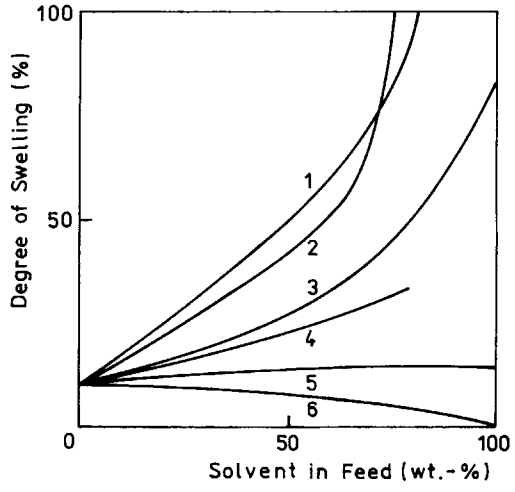

Figure 1 Dependence of degree of swelling of PPO homogeneous membrane on the composition of binary mixture ethanol–solvent: (1) trichloroethylene, (2) toluene, (3) 1,4-dioxane, (4) cyclohexane, (5) 1-propanol, (6) water.

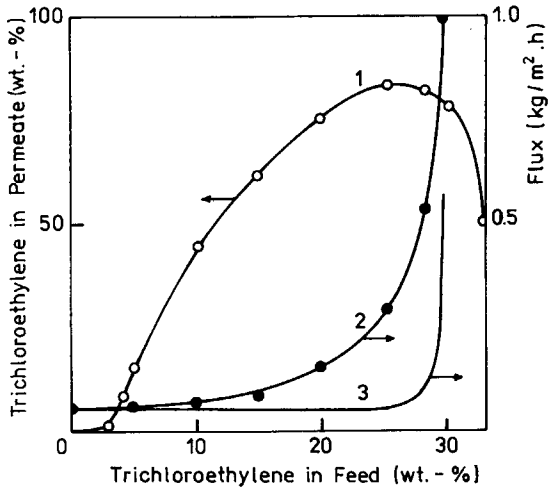

Figure 2 Dependence of trichloroethylene content in (1) permeate of (2) total flux and of (3) ethanol flux on trichloroethylene content in the feed mixture.

toward a PPO membrane are similar: their solubility parameters, δ, are 18.8 and 18.2 $MPa^{1/2}$, respectively, thus, of the same value as that of PPO[5] (δ = 18.5 $MPa^{1/2}$) and both dissolve PPO. The dependencies of trichloroethylene and toluene permeation on their concentration in the feed are shown in Figures 2 and 3 (curves 1). When their concentration in the feed mixture is low, the PPO membrane is (nearly) not swelled (Fig. 1) and smaller molecules of ethanol permeate it preferentially. If the concentration of trichloroethylene or toluene in the feed is increased up to a certain value (approx. 25 wt % for

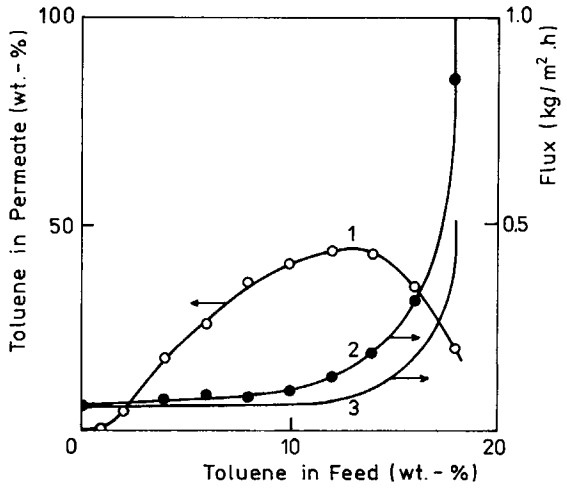

Figure 3 Dependence of toluene content in (1) permeate of (2) total flux and of (3) ethanol flux on toluene content in the feed mixture.

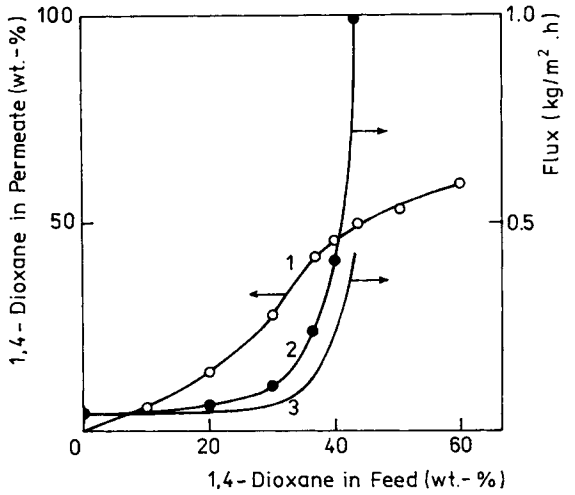

Figure 4 Dependence of 1,4-dioxane content in (1) permeate of (2) total flux and of (3) ethanol flux on 1,4-dioxane content in the feed mixture.

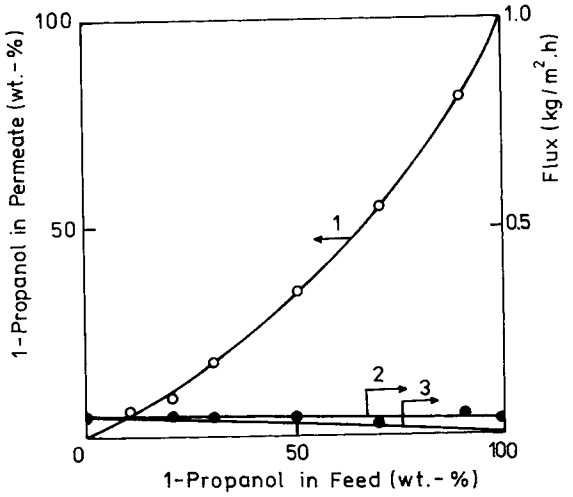

Figure 6 Dependence of 1-propanol content in (1) permeate of (2) total flux and of (3) ethanol flux on 1-propanol content in the feed mixture.

trichloroethylene and 12 wt % for toluene), the total flux through the membrane increases (curve 2) while the ethanol flux (curve 3) remains virtually constant. In this range of feed composition the membrane is permeated preferentially by a chemically similar liquid. When the concentration of trichloroethylene or toluene in the feed is further increased, the flux through the highly swollen membrane is dramatically increased but the membrane loses its selectivity.

If, on the contrary, the concentration of trichloroethylene or toluene in the feed is again decreased, the membrane does not deswell homogeneously, but a microporous membrane is formed in dependence on the previous state of swelling and the rate of the change. The selectivity of ethanol vs. trichloroethylene or toluene is then close to that given by the vapor–liquid equilibrium, and membrane distillation takes place.

The values of solubility parameters of cyclohexane (δ = 16.8 $MPa^{1/2}$) and 1,4-dioxane (20.5 $MPa^{1/2}$) are somewhat more remote from that of PPO, and the polymer is highly swelled by both pure

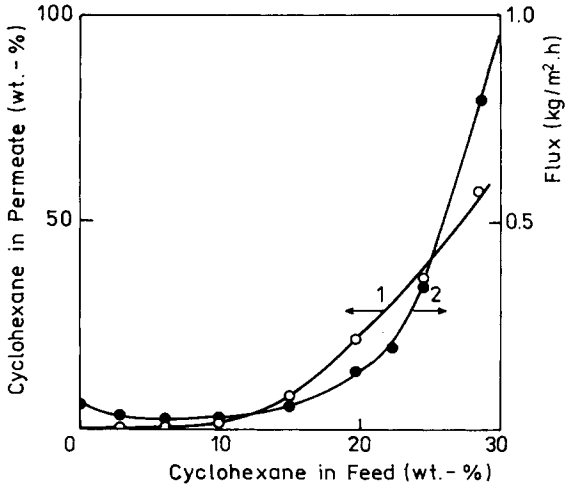

Figure 5 Dependence of cyclohexane content in (1) permeate and of (2) total flux on cyclohexane content in the feed mixture.

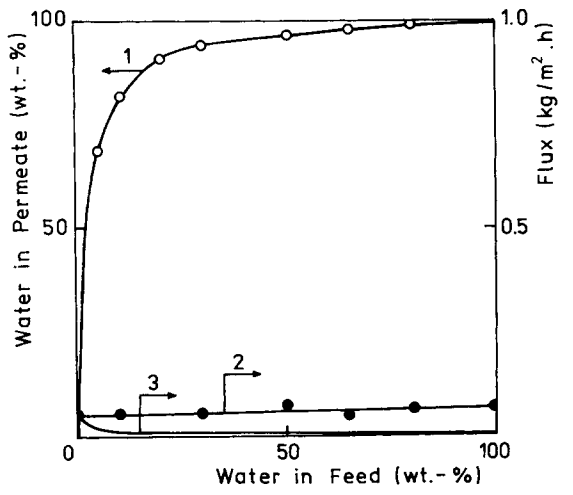

Figure 7 Dependence of water content in (1) permeate of (2) total flux and of (3) ethanol flux on water content in the feed mixture.

solvents. The dependence of the dioxane content in the permeate, of the total flux, and of the ethanol flux through the PPO membrane on the dioxane concentration in the feed is shown in Figure 4. It can be seen that the dioxane behavior during the pervaporation through the PPO membrane is similar to that of trichloroethylene and toluene but the trends are not so pronounced.

Cyclohexane shows an anomalous behavior: If it is added up to the amount of approx. 8 wt % to pure ethanol in feed, the membrane total flux decreases and cyclohexane virtually does not permeate the membrane at all. At higher concentrations, however, a distinct permeation enhancement takes place (Fig. 5).

The values of solubility parameters of 1-propanol (δ = 24.3 $MPa^{1/2}$) and water (δ = 47.39 $MPa^{1/2}$) are quite different from that of PPO, and the polymer is only slightly swelled by these solvents. The selectivity of the PPO membrane does not depend on 1-propanol or water concentration in the feed (Figs. 6 and 7) and is given clearly by the size of the permeating species: small molecules of water permeate the membrane at a higher rate and bigger molecules of 1-propanol at a lower rate than ethanol molecules.

CONCLUSIONS

If a liquid in the feed mixture has a strong affinity to poly(2,6-dimethyl-1,4-phenylene oxide), a typical glassy polymer, and its concentration is high enough, it permeates preferentially through the PPO pervaporation membrane. If the concentration of the liquid is low or the liquid has a low affinity to the membrane material, its affinity does not determine the membrane selectivity.

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